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(54) Title: PROCESS FOR MAKING A HIGH DENSITY DETERGENT COMPOSITION FROM A SURFACTANT PASTE CONTAIN-  
ING A NON-AQUEOUS BINDER

(57) Abstract

A process for preparing high density detergent agglomerates having a density of at least 650 g/l is provided. The process comprises the steps of: (a) continuously mixing a detergent surfactant paste and dry starting detergent material into a high speed mixer/densifier to obtain detergent agglomerates, wherein said surfactant paste includes, by weight of said surfactant paste, from about 0.1 % to about 50 % of a non-aqueous binder, from about 70 % to about 95 % of a detergative surfactant, and the balance water; (b) mixing the detergent agglomerates in a moderate speed mixer/densifier to further densify and agglomerate the detergent agglomerates; and (c) drying said detergent agglomerates so as to form the high density detergent composition. The process may include one or more additional processing steps such as adding a coating agent after the moderate speed mixer/densifier to facilitate and control agglomeration.

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PROCESS FOR MAKING A HIGH DENSITY DETERGENT COMPOSITION FROM A  
SURFACTANT PASTE CONTAINING A NON-AQUEOUS BINDER

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FIELD OF THE INVENTION

The present invention generally relates to a process for producing a high density detergent composition. More particularly, the invention is directed to a continuous process during which high density detergent agglomerates are produced by feeding a surfactant paste with a non-aqueous binder and adjunct dry starting detergent material into two serially positioned mixer/densifiers. The process produces a high density detergent composition with unexpectedly improved flow properties which can be commercially sold as a low dosage or "compact" detergent composition.

BACKGROUND OF THE INVENTION

Recently, there has been considerable interest within the detergent industry for laundry detergents which are "compact" and therefore, have low dosage volumes. To facilitate production of these so-called low dosage detergents, many attempts have been made to produce high bulk density detergents, for example with a density of 650 g/l or higher. The low dosage detergents are currently in high demand as they conserve resources and can be sold in small packages which are more convenient for consumers.

Generally, there are two primary types of processes by which detergent granules or powders can be prepared. The first type of process involves spray-drying an aqueous detergent slurry in a spray-drying tower to produce highly porous detergent granules. In the second type of process, the various detergent components are dry mixed after which they are agglomerated with a binder such as a nonionic or anionic surfactant. In both processes, the most important factors which govern the density of the resulting detergent granules are the density, porosity and surface area of the various starting materials and their respective chemical composition. These parameters, however, can only be varied within a limited range. Thus, a substantial bulk density increase only can be achieved by additional processing steps which lead to densification of the detergent granules.

There have been many attempts in the art for providing processes which increase the density of detergent granules or powders. Particular attention has been given to densification of spray-dried granules by post tower treatment. For example, one attempt involves a batch process in which spray-dried or granulated detergent powders containing sodium tripolyphosphate and sodium sulfate are densified and spheronized in a Marumerizer®. This apparatus comprises a substantially horizontal, roughened, rotatable table positioned within and at the base of a substantially vertical, smooth walled cylinder. This process, however, is essentially a batch process and is therefore less suitable for the large scale production of detergent powders. More recently, other attempts have been made to provide a continuous processes for increasing the density of "post-tower" or spray dried detergent

granules. Typically, such processes require a first apparatus which pulverizes or grinds the granules and a second apparatus which increases the density of the pulverized granules by agglomeration. These processes achieve the desired increase in density only by treating or densifying "post tower" or spray dried granules.

5           However, all of the aforementioned processes are directed primarily for densifying or otherwise processing spray dried granules. Currently, the relative amounts and types of materials subjected to spray drying processes in the production of detergent granules has been limited. For example, it has been difficult to attain high levels of surfactant in the resulting detergent composition, a feature which facilitates production of low dosage detergents. Thus, it would be  
10       desirable to have a process by which detergent compositions can be produced without having the limitations imposed by conventional spray drying techniques.

          To that end, the art is also replete with disclosures of processes which entail agglomerating detergent compositions. For example, attempts have been made to agglomerate detergent builders by mixing zeolite and/or layered silicates in a mixer to form free flowing agglomerates. While such  
15       attempts suggest that their process can be used to produce detergent agglomerates, they do not provide a mechanism by which starting detergent materials in the form of pastes, liquids and dry materials can be effectively agglomerated into crisp, free flowing detergent agglomerates having a high density. Further in this regard, previous agglomeration processes have significant room for improvement with respect to the flow properties of the agglomerates produced. Such flow properties  
20       which include free flowability, crispness, narrow particle size distributions and the like are necessary for modern day low dosage, compact detergent products. Additionally, previous agglomeration processes do not adequately account for, or are focused on minimizing the need for recycling undersized or over sized agglomerates produced from the process.

          Accordingly, there remains a need in the art to have a process for continuously producing a  
25       high density detergent composition directly from starting detergent ingredients. Also, there remains a need for a process which produces such a high density detergent composition having improved flow properties and minimizes the need for recycling. Finally, there remains a need for such a process which is more efficient and economical to facilitate large-scale production of low dosage or compact detergents.

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#### BACKGROUND ART

          The following references are directed to densifying spray-dried granules: Appel et al. U.S. Patent No. 5,133,924 (Lever); Bortolotti et al, U.S. Patent No. 5,160,657 (Lever); Johnson et al, British patent No. 1,517,713 (Unilever); and Curtis, European Patent Application 451,894. The following references are directed to producing detergents by agglomeration: Beerse et al, U.S. Patent  
35       No. 5,108,646 (Procter & Gamble); Capeci et al, U.S. Patent No. 5,366,652 (Procter & Gamble); Hollingsworth et al, European Patent Application 351,937 (Unilever); and Swatling et al, U.S. Patent No. 5,205,958.

### SUMMARY OF THE INVENTION

The present invention meets the aforementioned needs in the art by providing a process which produces a high density detergent composition in the form of agglomerates directly from a surfactant paste and adjunct dry starting detergent ingredients. The surfactant paste has a relatively low amount of water, but retains its transportability and processability by including a sufficient amount of a non-aqueous binder to which the formation of agglomerates having unexpectedly improved flow properties are attributed. As a consequence of these improved flow properties, the agglomerates exiting the instant process are less sticky and do not require recycling of oversized agglomerate particles back into the process to the extent of previous processes. The oversized agglomerate particles can be appropriately sized by more economical grinding processes subsequent to the instant process.

As used herein, the term "agglomerates" refers to particles formed by agglomerating more porous starting detergent ingredients (particles) which typically have a smaller median particle size than the formed agglomerates. All percentages and ratios used herein are expressed as percentages by weight (anhydrous basis) unless otherwise indicated. All documents are incorporated herein by reference. All viscosities referenced herein are measured at 70°C ( $\pm 5^\circ\text{C}$ ) and at shear rates of about 10 to 100  $\text{sec}^{-1}$ .

In accordance with one aspect of the invention, a process for preparing a crisp, free flowing, high density detergent composition is provided. The process comprises the steps of: (a) continuously mixing a detergent surfactant paste and dry starting detergent material into a high speed mixer/densifier to obtain detergent agglomerates, wherein the surfactant paste includes, by weight of the surfactant paste, from about 0.1% to about 50% of a non-aqueous binder, from about 30% to about 95% of a deterative surfactant, and the balance water; (b) mixing the detergent agglomerates in a moderate speed mixer/densifier to further densify and agglomerate the detergent agglomerates; and (c) drying the detergent agglomerates so as to form the high density detergent composition.

In an especially preferred embodiment of the invention, the process comprises the steps of: (a) continuously mixing a detergent surfactant paste and a dry starting detergent material comprising a builder selected from the group consisting of aluminosilicates, crystalline layered silicates, sodium carbonate,  $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ ,  $\text{K}_2\text{Ca}(\text{CO}_3)_2$ ,  $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ ,  $\text{NaKCa}(\text{CO}_3)_2$ ,  $\text{NaKCa}_2(\text{CO}_3)_3$ ,  $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ , and mixtures thereof, into a high speed mixer/densifier to obtain detergent agglomerates, wherein said surfactant paste includes, by weight of said surfactant paste, from about 0.1% to about 50% of a non-aqueous binder, from about 30% to about 95% of a deterative surfactant, and the balance water, the weight ratio of the surfactant paste to the dry detergent material is from about 1:10 to about 10:1; (b) mixing the detergent agglomerates in a moderate speed mixer/densifier to further densify and agglomerate the detergent agglomerates; (c) drying the detergent agglomerates; and (d) adding a coating agent to obtain the high density detergent composition having a density of at least 650 g/l.

The invention also provides a high density detergent composition made according to the process of the invention and its various embodiments.

Accordingly, it is an object of the present invention to provide a process for continuously producing a high density detergent composition directly from a surfactant paste and adjunct dry starting detergent ingredients. It is also an object of the invention to provide such a process which produces a composition exhibiting improved flow properties. Also, it is an object of the invention to produce such a process which is more efficient and economical to operate on a large scale. These and other objects, features and attendant advantages of the present invention will become apparent to those skilled in the art from a reading of the following drawing, detailed description of the preferred embodiment and the appended claims.

#### BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a flow chart illustrating a preferred process in which two agglomerating mixer/densifiers, fluid bed dryer, fluid bed cooler and screening apparatus are serially positioned in accordance with the invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present process is used in the production of low dosage detergent agglomerates directly from starting detergent ingredients rather than conventional "post-tower" detergent granules. By "post-tower" detergent granules, we mean those detergent granules which have been processed through a conventional spray-drying tower or similar apparatus. The process of the invention allows for production of low dosage detergents in an environmentally conscious manner in that the use of spray drying techniques and the like which typically emit pollutants through their towers or stacks into the atmosphere is eliminated. This feature of the process invention is extremely desirable in geographic areas which are especially sensitive to emission of pollutants into the atmosphere.

#### Process

Reference is now made to Fig. 1 which presents a flow chart illustrating the instant process and various embodiments thereof. In the first step of the process, the invention entails continuously mixing into a high speed mixer/densifier 10 several streams of starting detergent ingredients including a surfactant paste stream 12 and a dry starting detergent material stream 14. The surfactant paste 12 preferably comprises from about 30% to about 95%, preferably from about 60% to about 85% and, most preferably from about 70% to about 75%, by weight of a detergent surfactant in paste form.

Preferably, surfactant paste 12 includes a non-aqueous binder to facilitate production of high density detergent agglomerates with improved flow properties. It has been found that by including a non-aqueous binder in the surfactant paste 12 which at least partially replaces the water in the paste surprisingly results in the formation of agglomerates having substantially improved flow properties. The non-aqueous binder in the paste not only improves the agglomerates ultimately formed by the instant process, but also retains the processability and transportability of the paste in

that the viscosity remains low enough for such tasks. While not intending to be bound by theory, it is believed that partial replacement of the water in the paste by the non-aqueous binder renders agglomeration to occur at a higher temperature and to be more controllable resulting in the formation of more crisp, free flowing agglomerates.

5 Accordingly, the surfactant paste also comprises from about 0.1% to about 50%, more preferably from about 1% to about 15%, and most preferably from about 2% to about 8%, by weight of the non-aqueous binder and the balance water, and optionally, other conventional detergent ingredients. The binder enhances agglomeration by providing a "binding" or "sticking" agent for the detergent components in the process. While the particular binder need only be non-aqueous in  
10 nature, it preferably has a viscosity of from about 100 cps to about 100,000 cps, most preferably from about 1000 cps to about 25,000 cps. Also, it is preferable for the binder to have a melting point of from about 35 °C to about 70 °C, most preferably of from about 40 °C to about 60 °C, so that it can operate most effectively in the instant process. The binder is preferably selected from the group consisting of anionic surfactants, nonionic surfactants, polyethylene glycol, polyvinyl pyrrolidone  
15 polyacrylates, citric acid and mixtures thereof. The most preferable binder is polyethylene glycol. Other suitable binder materials including those listed herein are described in Beerse et al, U.S. Patent No. 5,108,646 (Procter & Gamble Co.), the disclosure of which is incorporated herein by reference.

Preferably, the dry starting detergent material 14 comprises from about 20% to about 50%, preferably from about 25% to about 45% and, most preferably from about 30% to about 40% of an  
20 aluminosilicate or zeolite builder, and from about 10% to about 40%, preferably from about 15% to about 30% and, most preferably from about 15% to about 25% of a sodium carbonate. Most preferably, the builder is selected from the group consisting of aluminosilicates, crystalline layered silicates, sodium carbonate,  $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ ,  $\text{K}_2\text{Ca}(\text{CO}_3)_2$ ,  $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ ,  $\text{NaKCa}(\text{CO}_3)_2$ ,  $\text{NaKCa}_2(\text{CO}_3)_3$ ,  $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ , and mixtures thereof. It should be understood that additional  
25 starting detergent ingredients several of which are described hereinafter may be mixed into high speed mixer/densifier 10 without departing from the scope of the invention.

Preferably, the ratio of the surfactant paste 12 to the dry starting detergent material 14 is from about 1:10 to about 10:1, more preferably from about 1:4 to about 4:1 and, most preferably from about 2:1 to about 2:3.

30 It has been found that the first processing step can be successfully completed, under the process parameters described herein, in a high speed mixer/densifier 10 which preferably is a Lödige CB mixer or similar brand mixer. These types of mixers essentially consist of a horizontal, hollow static cylinder having a centrally mounted rotating shaft around which several plough-shaped blades are attached. Preferably, the shaft rotates at a speed of from about 100 rpm to about 2500 rpm, more  
35 preferably from about 300 rpm to about 1600 rpm. Preferably, the mean residence time of the detergent ingredients in the high speed mixer/densifier 10 is preferably in range from about 2 seconds to about 45 seconds, and most preferably from about 5 seconds to about 15 seconds.

The resulting detergent agglomerates formed in the high speed mixer/densifier 10 are then fed into a lower or moderate speed mixer/densifier 16 during which further agglomeration and densification is carried forth. This particular moderate speed mixer/densifier 16 used in the present process should include liquid distribution and agglomeration tools so that both techniques can be carried forth simultaneously. It is preferable to have the moderate speed mixer/densifier 16 to be, for example, a Lödige KM (Ploughshare) mixer, Drais® K-T 160 mixer or similar brand mixer. The residence time in the moderate speed mixer/densifier 16 is preferably from about 0.5 minutes to about 15 minutes, most preferably the residence time is about 1 to about 10 minutes. The liquid distribution is accomplished by cutters, generally smaller in size than the rotating shaft, which preferably operate at about 3600 rpm.

In accordance with the present process, the high speed mixer/densifier 10 and moderate speed mixer/densifier 16 in combination preferably impart a requisite amount of energy to form the desired agglomerates. More particularly, the moderate speed mixer/densifier imparts from about  $5 \times 10^{10}$  erg/kg to about  $2 \times 10^{12}$  erg/kg at a rate of from about  $3 \times 10^8$  erg/kg-sec to about  $3 \times 10^9$  erg/kg-sec to form free flowing high density detergent agglomerates. The energy input and rate of input can be determined by calculations from power readings to the moderate speed mixer/densifier with and without granules, residence time of the granules in the mixer/densifier, and the mass of the granules in the mixer/densifier. Such calculations are clearly within the scope of the skilled artisan.

The density of the resulting detergent agglomerates exiting the moderate speed mixer/densifier 16 is at least 650 g/l, more preferably from about 700 g/l to about 875 g/l. Thereafter, the detergent agglomerates are dried in a fluid bed dryer 18 or similar apparatus to obtain the high density granular detergent composition which is ready for packaging and sale as a low dosage, compact detergent product at this point. The detergent agglomerates produced by the process preferably have a surfactant level of from about 25% to about 55%, more preferably from about 35% to about 55% and, most preferably from about 45% to about 55%. The particle porosity of the resulting detergent agglomerates of the composition is preferably in a range from about 5% to about 20%, more preferably at about 10%. As those skilled in the art will readily appreciate, a low porosity detergent agglomerate provides a dense or low dosage detergent product, to which the present process is primarily directed.

In addition, an attribute of dense or densified detergent agglomerates is the relative particle size. The present process typically provides agglomerates having a median particle size of from about 400 microns to about 700 microns, and more preferably from about 400 microns to about 500 microns. As used herein, the phrase "median particle size" refers to individual agglomerates and not individual particles or detergent granules. The combination of the above-referenced porosity and particle size results in agglomerates having density values of 650 g/l and higher. Such a feature is especially useful in the production of low dosage laundry detergents as well as other granular compositions such as dishwashing compositions.



### Optional Process Steps

In an optional step of the present process, the detergent agglomerates exiting the fluid bed dryer 18 are further conditioned by cooling the agglomerates in a fluid bed cooler 20 or similar apparatus as are well known in the art. Another optional process step involves adding a coating agent to improve flowability and/or minimize over agglomeration of the detergent composition in one or more of the following locations of the instant process: (1) the coating agent can be added directly after the fluid bed cooler 20 as shown by coating agent stream 22 (preferred); (2) the coating agent may be added between the fluid bed dryer 18 and the fluid bed cooler 20 as shown by coating agent stream 24; (3) the coating agent may be added between the fluid bed dryer 18 and the moderate speed mixer/densifier 16 as shown by stream 26; and/or (4) the coating agent may be added directly to the moderate speed mixer/densifier 16 and the fluid bed dryer 18 as shown by stream 28. It should be understood that the coating agent can be added in any one or a combination of streams 22, 24, 26, and 28 as shown in Fig. 1. The coating agent stream 22 is the most preferred in the instant process. The coating agent is preferably selected from the group consisting of aluminosilicates, silicates, carbonates and mixtures thereof. The coating agent not only enhances the free flowability of the resulting detergent composition which is desirable by consumers in that it permits easy scooping of detergent during use, but also serves to control agglomeration by preventing or minimizing over agglomeration, especially when added directly to the moderate speed mixer/densifier 16. As those skilled in the art are well aware, over agglomeration can lead to very undesirable flow properties and aesthetics of the final detergent product.

Other optional steps contemplated by the present process include screening the oversized detergent agglomerates in a screening apparatus 30 which can take a variety of forms including but not limited to conventional screens chosen for the desired particle size of the finished detergent product. Other optional steps include conditioning of the detergent agglomerates by subjecting the agglomerates to additional drying. Optionally, the process can comprise the step of spraying an additional binder in one or both of the mixer/densifiers 10 and 16. The binder can comprise the same non-aqueous binder materials used in the surfactant paste described previously.

Another optional step of the instant process entails finishing the resulting detergent agglomerates by a variety of processes including spraying and/or admixing other conventional detergent ingredients, collectively referenced as the finishing step 32 in Fig. 1. For example, the finishing step encompasses spraying perfumes, brighteners and enzymes onto the finished agglomerates to provide a more complete detergent composition. Such techniques and ingredients are well known in the art.

### Detergent Surfactant Paste

As described briefly previously, the detergent surfactant paste used in the process is preferably in the form of a non-aqueous viscous paste. This so-called viscous surfactant paste has a viscosity of from about 5,000 cps to about 100,000 cps, more preferably from about 10,000 cps to

about 80,000 cps. The viscosity is measured at 70°C and at shear rates of about 10 to 100 sec.<sup>-1</sup>.

The surfactant itself, in the viscous surfactant paste, is preferably selected from anionic, nonionic, zwitterionic, ampholytic and cationic classes and compatible mixtures thereof. Detergent surfactants useful herein are described in U.S. Patent 3,664,961, Norris, issued May 23, 1972, and in  
 5 U.S. Patent 3,919,678, Laughlin et al., issued December 30, 1975, both of which are incorporated herein by reference. Useful cationic surfactants also include those described in U.S. Patent 4,222,905, Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980, both of which are also incorporated herein by reference. Of the surfactants, anionics and nonionics are preferred and anionics are most preferred.

10 Nonlimiting examples of the preferred anionic surfactants useful in the surfactant paste include the conventional C<sub>11</sub>-C<sub>18</sub> alkyl benzene sulfonates ("LAS"), primary, branched-chain and random C<sub>10</sub>-C<sub>20</sub> alkyl sulfates ("AS"), the C<sub>10</sub>-C<sub>18</sub> secondary (2,3) alkyl sulfates of the formula CH<sub>3</sub>(CH<sub>2</sub>)<sub>x</sub>(CHOSO<sub>3</sub><sup>-</sup>M<sup>+</sup>)CH<sub>3</sub> and CH<sub>3</sub>(CH<sub>2</sub>)<sub>y</sub>(CHOSO<sub>3</sub><sup>-</sup>M<sup>+</sup>)CH<sub>2</sub>CH<sub>3</sub> where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation,  
 15 especially sodium, unsaturated sulfates such as oleyl sulfate, and the C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy sulfates ("AE<sub>x</sub>S"; especially EO 1-7 ethoxy sulfates).

Optionally, other exemplary surfactants useful in the paste of the invention include and C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C<sub>10</sub>-18 glycerol ethers, the C<sub>10</sub>-C<sub>18</sub> alkyl polyglycosides and their corresponding sulfated polyglycosides, and  
 20 C<sub>12</sub>-C<sub>18</sub> alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C<sub>12</sub>-C<sub>18</sub> alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C<sub>6</sub>-C<sub>12</sub> alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C<sub>12</sub>-C<sub>18</sub> betaines and sulfobetaines ("sultaines"), C<sub>10</sub>-C<sub>18</sub> amine oxides, and the like, can also be included in the overall compositions. The C<sub>10</sub>-C<sub>18</sub> N-alkyl polyhydroxy fatty acid  
 25 amides can also be used. Typical examples include the C<sub>12</sub>-C<sub>18</sub> N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C<sub>10</sub>-C<sub>18</sub> N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C<sub>12</sub>-C<sub>18</sub> glucamides can be used for low sudsing. C<sub>10</sub>-C<sub>20</sub> conventional soaps may also be used. If high sudsing is desired, the branched-chain C<sub>10</sub>-C<sub>16</sub> soaps may be used. Mixtures of anionic and  
 30 nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

#### Dry Detergent Material

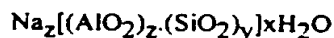
The starting dry detergent material of the present process preferably comprises a detergent aluminosilicate builder which are referenced as aluminosilicate ion exchange materials and sodium  
 35 carbonate. The aluminosilicate ion exchange materials used herein as a detergent builder preferably have both a high calcium ion exchange capacity and a high exchange rate. Without intending to be limited by theory, it is believed that such high calcium ion exchange rate and capacity are a function of

several interrelated factors which derive from the method by which the aluminosilicate ion exchange material is produced. In that regard, the aluminosilicate ion exchange materials used herein are preferably produced in accordance with Corkill et al, U.S. Patent No. 4,605,509 (Procter & Gamble), the disclosure of which is incorporated herein by reference.

5 Preferably, the aluminosilicate ion exchange material is in "sodium" form since the potassium and hydrogen forms of the instant aluminosilicate do not exhibit the as high of an exchange rate and capacity as provided by the sodium form. Additionally, the aluminosilicate ion exchange material preferably is in over dried form so as to facilitate production of crisp detergent agglomerates as described herein. The aluminosilicate ion exchange materials used herein preferably have particle size  
10 diameters which optimize their effectiveness as detergent builders. The term "particle size diameter" as used herein represents the average particle size diameter of a given aluminosilicate ion exchange material as determined by conventional analytical techniques, such as microscopic determination and scanning electron microscope (SEM). The preferred particle size diameter of the aluminosilicate is from about 0.1 micron to about 10 microns, more preferably from about 0.5 microns to about 9 microns.

15 Most preferably, the particle size diameter is from about 1 microns to about 8 microns.

Preferably, the aluminosilicate ion exchange material has the formula



wherein z and y are integers of at least 6, the molar ratio of z to y is from about 1 to about 5 and x is from about 10 to about 264. More preferably, the aluminosilicate has the formula



wherein x is from about 20 to about 30, preferably about 27. These preferred aluminosilicates are available commercially, for example under designations Zeolite A, Zeolite B and Zeolite X.

Alternatively, naturally-occurring or synthetically derived aluminosilicate ion exchange materials suitable for use herein can be made as described in Krummel et al, U.S. Patent No. 3,985,669, the  
25 disclosure of which is incorporated herein by reference.

The aluminosilicates used herein are further characterized by their ion exchange capacity which is at least about 200 mg equivalent of  $\text{CaCO}_3$  hardness/gram, calculated on an anhydrous basis, and which is preferably in a range from about 300 to 352 mg equivalent of  $\text{CaCO}_3$  hardness/gram. Additionally, the instant aluminosilicate ion exchange materials are still further characterized by their  
30 calcium ion exchange rate which is at least about 2 grains  $\text{Ca}^{++}$ /gallon/minute/-gram/gallon, and more preferably in a range from about 2 grains  $\text{Ca}^{++}$ /gallon/minute/-gram/gallon to about 6 grains  $\text{Ca}^{++}$ /gallon/minute/-gram/gallon.

Another very viable builder material which can also be used as the coating agent in the process as described previously include materials having the formula  $(\text{M}_x)_i \text{Ca}_y (\text{CO}_3)_z$  wherein x and i are  
35 integers from 1 to 15, y is an integer from 1 to 10, z is an integer from 2 to 25,  $\text{M}_i$  are cations, at least one of which is a water-soluble, and the equation  $\sum_i = 1-15(x_i \text{ multiplied by the valence of } \text{M}_i) + 2y = 2z$  is satisfied such that the formula has a neutral or "balanced" charge. Waters of hydration or anions other

than carbonate may be added provided that the overall charge is balanced or neutral. The charge or valence effects of such anions should be added to the right side of the above equation.

Preferably, there is present a water-soluble cation selected from the group consisting of hydrogen, water-soluble metals, hydrogen, boron, ammonium, silicon, and mixtures thereof, more preferably, sodium, potassium, hydrogen, lithium, ammonium and mixtures thereof, sodium and potassium being highly preferred. Nonlimiting examples of noncarbonate anions include those selected from the group consisting of chloride, sulfate, fluoride, oxygen, hydroxide, silicon dioxide, chromate, nitrate, borate and mixtures thereof. Preferred builders of this type in their simplest forms are selected from the group consisting of  $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ ,  $\text{K}_2\text{Ca}(\text{CO}_3)_2$ ,  $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ ,  $\text{NaKCa}(\text{CO}_3)_2$ ,  $\text{NaKCa}_2(\text{CO}_3)_3$ ,  $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ , and combinations thereof. An especially preferred material for the builder described herein is  $\text{Na}_2\text{Ca}(\text{CO}_3)_2$  in any of its crystalline modifications.

Suitable builders of the above-defined type are further illustrated by, and include, the natural or synthetic forms of any one or combinations of the following minerals: Afghanite, Andersonite, AshcroftineY, Beyerite, Borcarite, Burbankite, Butschliite, Cancrinite, Carboceimaite, Carletonite, Davyne, DonnayiteY, Fairchildite, Ferrisurite, Franzinite, Gaudefroyite, Gaylussite, Girvasite, Gregoryite, Jouravskite, KamphaugiteY, Kettnerite, Khanneshite, LepersonniteGd, Liontite, McKelveyiteY, Microsommitte, Mroseite, Natrofairchildite, Nyerereite, RemonditeCe, Sacrofanite, Schrockingerite, Shortite, Surite, Tunisite, Tuscanite, Tyrolite, Vishnevite, and Zemkorite. Preferred mineral forms include Nyerereite, Fairchildite and Shortite.

#### 20 Adjunct Detergent Ingredients

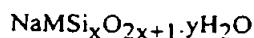
The starting dry detergent material in the present process can include additional detergent ingredients and/or, any number of additional ingredients can be incorporated in the detergent composition during subsequent steps of the present process. These adjunct ingredients include other detergency builders, bleaches, bleach activators, suds boosters or suds suppressers, anti-tarnish and anticorrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, smectite clays, enzymes, enzyme-stabilizing agents and perfumes. See U.S. Patent 3,936,537, issued February 3, 1976 to Baskerville, Jr. et al., incorporated herein by reference.

Other builders can be generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, borates, polyhydroxy sulfonates, polyacetates, carboxylates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of the above. Preferred for use herein are the phosphates, carbonates,  $\text{C}_{10-18}$  fatty acids, polycarboxylates, and mixtures thereof. More preferred are sodium tripolyphosphate, tetrasodium pyrophosphate, citrate, tartrate mono- and di-succinates, and mixtures thereof (see below).

In comparison with amorphous sodium silicates, crystalline layered sodium silicates exhibit a clearly increased calcium and magnesium ion exchange capacity. In addition, the layered sodium

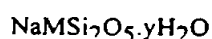
silicates prefer magnesium ions over calcium ions, a feature necessary to insure that substantially all of the "hardness" is removed from the wash water. These crystalline layered sodium silicates, however, are generally more expensive than amorphous silicates as well as other builders. Accordingly, in order to provide an economically feasible laundry detergent, the proportion of crystalline layered sodium silicates used must be determined judiciously.

The crystalline layered sodium silicates suitable for use herein preferably have the formula



wherein M is sodium or hydrogen, x is from about 1.9 to about 4 and y is from about 0 to about 20.

More preferably, the crystalline layered sodium silicate has the formula



wherein M is sodium or hydrogen, and y is from about 0 to about 20. These and other crystalline layered sodium silicates are discussed in Corkill et al, U.S. Patent No. 4,605,509, previously incorporated herein by reference.

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphates. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1, 1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, all of which are incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are tetraborate decahydrate and silicates having a weight ratio of  $\text{SiO}_2$  to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Polymeric polycarboxylate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, the disclosure of which is incorporated herein by reference. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylene malonic acid. Some of these materials are useful as the water-soluble anionic polymer as hereinafter described, but only if in intimate admixture with the non-soap anionic surfactant.

Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al, and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al, both of which are incorporated herein by reference. These

polyacetal carboxylates can be prepared by bringing together under polymerization conditions an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a detergent composition. Particularly preferred polycarboxylate builders are the ether carboxylate builder compositions comprising a combination of tartrate monosuccinate and tartrate disuccinate described in U.S. Patent 4,663,071, Bush et al., issued May 5, 1987, the disclosure of which is incorporated herein by reference.

Bleaching agents and activators are described in U.S. Patent 4,412,934, Chung et al., issued November 1, 1983, and in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, both of which are incorporated herein by reference. Chelating agents are also described in U.S. Patent 4,663,071, Bush et al., from Column 17, line 54 through Column 18, line 68, incorporated herein by reference. Suds modifiers are also optional ingredients and are described in U.S. Patents 3,933,672, issued January 20, 1976 to Bartoletta et al., and 4,136,045, issued January 23, 1979 to Gault et al., both incorporated herein by reference.

Suitable smectite clays for use herein are described in U.S. Patent 4,762,645, Tucker et al., issued August 9, 1988, Column 6, line 3 through Column 7, line 24, incorporated herein by reference. Suitable additional detergency builders for use herein are enumerated in the Baskerville patent, Column 13, line 54 through Column 16, line 16, and in U.S. Patent 4,663,071, Bush et al, issued May 5, 1987, both incorporated herein by reference.

In order to make the present invention more readily understood, reference is made to the following examples, which are intended to be illustrative only and not intended to be limiting in scope.

#### EXAMPLE I

This Example illustrates the process of the invention which produces free flowing, crisp, high density detergent composition in the form of agglomerates. Two feed streams of various detergent starting ingredients are continuously fed, at a rate of 1270 kg/hr, into a Lödige CB-30 mixer/densifier, one of which comprises a surfactant paste containing surfactant and the non-aqueous binder, polyethylene glycol, and the other stream containing starting dry detergent material containing aluminosilicate and sodium carbonate. The rotational speed of the shaft in the Lödige CB-30 mixer/densifier is about 1400 rpm and the mean residence time is about 10 seconds. The contents from the Lödige CB-30 mixer/densifer are continuously fed into a Lödige KM 600 mixer/densifer for further agglomeration during which the mean residence time is about 6 minutes. The resulting detergent agglomerates are then fed to a fluid bed dryer and then to a fluid bed cooler, the mean residence time being about 10 minutes and 15 minutes, respectively. A coating agent, aluminosilicate, is fed about midway down the moderate speed mixer/densifier 16 to control and prevent over agglomeration. The detergent agglomerates are then screened with conventional

screening apparatus resulting in a uniform particle size distribution. The composition of the detergent agglomerates exiting the fluid bed cooler is set forth in Table I below:

**TABLE I**

	<u>Component</u>	<u>% Weight of Total Feed</u>
5	C <sub>14-15</sub> alkyl sulfate	22.5
	C <sub>12.3</sub> linear alkylbenzene sulfonate	2.5
	Aluminosilicate	35.2
	Sodium carbonate	21.0
	Polyethylene glycol (MW 4000)	1.5
10	Misc. (water, etc.)	<u>12.3</u>
		100.0

Additional detergent ingredients including perfumes, enzymes, and other minors are sprayed onto the agglomerates described above in the finishing step to result in a finished detergent composition which is admixed with spray dried granules in a 60:40 weight ratio (agglomerates: spray dried granules). The relative proportions of the overall finished detergent composition produced by the process of instant process is presented in Table II below:

**TABLE II**

<u>Component</u>	<u>(% weight)</u>
C <sub>14-15</sub> alkyl sulfate/C <sub>12.3</sub> linear alkylbenzene sulfonate	16.3
Neodol 23-9.5 <sup>1</sup>	1.8
Polyacrylate (MW=4500)	3.2
Polyethylene glycol (MW=4000)	1.7
Sodium Sulfate	5.7
Aluminosilicate	26.3
Sodium carbonate	33.1
Protease enzyme	0.4
Amylase enzyme	0.1
Lipase enzyme	0.2
Cellulase enzyme	0.1
Minors (water, perfume, etc.)	<u>11.1</u>
	100.0

<sup>1</sup> C<sub>12-13</sub> alkyl ethoxylate (EO= 9) commercially available from Shell Oil Company.

The density of the resulting fully formulated detergent composition is 561 g/l, the median particle size is 450 microns. The density of the agglomerates alone is 810 g/l.

**EXAMPLE II**

This Example illustrates another process in accordance with the invention in which the steps described in Example I are performed except the coating agent, aluminosilicate, is added after the fluid bed cooler as opposed to in the moderate speed mixer/densifier. The composition of the detergent agglomerates exiting the fluid bed cooler after the coating agent is added is set forth in

5 Table III below:

**TABLE III**

	<u>Component</u>	<u>% Weight of Total Feed</u>
	C <sub>14-15</sub> alkyl sulfate	22.7
	C <sub>12-13</sub> linear alkylbenzene sulfonate	7.6
10	Aluminosilicate	34.5
	Sodium carbonate	21.2
	Polyethylene glycol (MW 4000)	1.5
	Misc. (water, perfume, etc.)	<u>12.5</u>
		100.0

15 Additional detergent ingredients including perfumes, brighteners and enzymes are sprayed onto the agglomerates described above in the finishing step to result in a finished detergent composition which is admixed with spray dried granules in a 60:40 weight ratio (agglomerates: spray dried granules). The relative proportions of the overall finished detergent composition produced by the process of instant process is presented in Table IV below:



**TABLE IV**

<u>Component</u>	<u>(% weight)</u>
C <sub>14-15</sub> alkyl sulfate/C <sub>12-13</sub> linear alkylbenzene sulfonate	16.3
Neodol 23-9.5 <sup>1</sup>	1.8
Polyacrylate (MW=4500)	3.2
Polyethylene glycol (MW=4000)	1.7
Sodium Sulfate	5.7
Aluminosilicate	26.3
Sodium carbonate	33.1
Protease enzyme	0.4
Amylase enzyme	0.1
Lipase enzyme	0.2
Cellulase enzyme	0.1
Minors (water, perfume, etc.)	<u>11.1</u>
	100.0

<sup>1</sup> C<sub>12-13</sub> alkyl ethoxylate (EO= 9) commercially available from Shell Oil Company.

The density of the resulting detergent composition is 560 g/l, the median particle size is 450 microns. The density of the agglomerates alone is 860 g/l.

5 Having thus described the invention in detail, it will be clear to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

What is claimed is:

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1. A process for continuously preparing high density detergent composition characterized by the steps of:
  - (a) continuously mixing a detergent surfactant paste and dry starting detergent material into a high speed mixer/densifier to obtain detergent agglomerates, wherein said surfactant paste includes, by weight of said surfactant paste, from 0.1% to 50% of a non-aqueous binder, from 30% to 95% of a deterative surfactant, and the balance water;
  - (b) mixing said detergent agglomerates in a moderate speed mixer/densifier to further densify and agglomerate said detergent agglomerates; and
  - (c) drying said detergent agglomerates so as to form said high density detergent composition.
2. The process according to claim 1 wherein said dry starting material is characterized by a builder selected from the group consisting of aluminosilicates, crystalline layered silicates, sodium carbonate,  $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ ,  $\text{K}_2\text{Ca}(\text{CO}_3)_2$ ,  $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ ,  $\text{NaKCa}(\text{CO}_3)_2$ ,  $\text{NaKCa}_2(\text{CO}_3)_3$ ,  $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ , and mixtures thereof.
3. The process according to claims 1-2 wherein said binder has a viscosity of 100 cps and 100,000 cps.
4. The process according to claims 1-3 further characterized by the step of adding a coating agent after said moderate speed mixer/densifier, wherein said coating agent is selected from the group consisting of aluminosilicates, carbonates, silicates and mixtures thereof.
5. The process according to claims 1-4 wherein said binder is selected from the group consisting of anionic surfactants, nonionic surfactants, polyethylene glycol, polyvinyl pyrrolidone, polyacrylates, citric acid and mixtures thereof.
6. The process according to claims 1-5 wherein the mean residence time of said detergent agglomerates in said high speed mixer/densifier is in range from 2 seconds to 45 seconds.
7. The process according to claims 1-6 wherein the mean residence time of said detergent agglomerates in said moderate speed mixer/densifier is in range from 0.5 minutes to 15 minutes.
8. The process according to claims 1-7 wherein said binder is polyethylene glycol.

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9. The process according to claims 1-8 wherein said binder has a melting point temperature of from 35 °C to 70 °C.
10. A process for continuously preparing high density detergent composition characterized by the steps of:
- (a) continuously mixing a detergent surfactant paste and a dry starting detergent material characterized by a builder selected from the group consisting of aluminosilicates, crystalline layered silicates, sodium carbonate,  $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ ,  $\text{K}_2\text{Ca}(\text{CO}_3)_2$ ,  $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ ,  $\text{NaKCa}(\text{CO}_3)_2$ ,  $\text{NaKCa}_2(\text{CO}_3)_3$ ,  $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ , and mixtures thereof, into a high speed mixer/densifier to obtain detergent agglomerates, wherein said surfactant paste includes, by weight of said surfactant paste, from 0.1% to 50% of a non-aqueous binder, from 70% to 95% of a deterative surfactant, and the balance water, the weight ratio of said surfactant paste to said dry detergent material is from 1:10 to 10:1;
  - (b) mixing said detergent agglomerates in a moderate speed mixer/densifier to further densify and agglomerate said detergent agglomerates;
  - (c) drying said detergent agglomerates; and
  - (d) adding a coating agent to obtain said high density detergent composition having a density of at least 650 g/l.

# INTERNATIONAL SEARCH REPORT

Internatic Application No  
PCT/US 96/14279

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C11D17/06 C11D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO 95 32276 A (PROCTER & GAMBLE) 30 November 1995 see the whole document ---	1-10
A	US 5 431 857 A (CAPECI SCOTT W) 11 July 1995 see column 5, line 15 - column 6, line 16; claims; examples ---	1-3,5-9
A	WO 95 10595 A (PROCTER & GAMBLE) 20 April 1995 see page 4, line 30 - page 7, line 8; claims; example 1 --- -/--	1-5,8,9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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- \*E\* earlier document but published on or after the international filing date
- \*I\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

14 January 1997

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# INTERNATIONAL SEARCH REPORT

Internat. Application No. PCT/US 96/14279
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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 06109 A (PROCTER & GAMBLE) 2 March 1995 cited in the application see page 4, line 10 - page 6, line 14; claims	1-3,5,8, 9
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A	WO 93 25378 A (PROCTER & GAMBLE) 23 December 1993 see page 8, line 3 - line 30; claims; example 1	1-3,6,7
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat Application No

PCT/US 96/14279

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		NO-A- 944840	06-02-95